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existing species it characterizes the *Camelidæ*, occurring also, as shown in *Palauchenia*, in the fossil form of that family; but this rare disposition of the vertebral arteries was likewise met with in a large fossil Ungulate of South America, *Macrauchenia*, belonging to the Perissodactyle group\*.

The author therefore communicates, as an appendix to his former paper on *Palauchenia*, a description, with drawings, of the mandibular dentition of *Macrauchenia patagonica*, of the natural size, the lower jaw of that fossil animal being still a unique specimen in the British Museum. It displays the entire molar series, with the exception of the first small premolar: the several teeth in place are described in detail and compared with those of other Perissodactyles. The grinding-surface of the true molars presents the bilobed or bicrescentic type, as in *Palæotherium* and *Rhinoceros*; but *Macrauchenia* differs from both those genera in the limitation of the assumption of the molar type to the last premolar, the antecedent ones retaining the single-lobed crown. From *Palæotherium* it further differs in the last molar being bilobed, as in *Rhinoceros*, not trilobed. In *Palauchenia* all the premolars have the simpler structure, as in Artiodactyles generally. *Macrauchenia* resembles *Anoplotherium* and *Dichodon* in retaining the typical dentition,  $i \frac{3-3}{3-3}$ ,  $c \frac{1-1}{1-1}$ ,  $p \frac{4-4}{4-4}$ ,  $m \frac{3-3}{3-3} = 44$ , and in the uninterrupted course of the dental series, not any of the teeth having a crown much higher or longer than the rest.

The paper is illustrated by drawings.

### III. "Researches into the Chemical Constitution of the Opium Bases. Part I.—On the Action of Hydrochloric Acid on Morphia." By AUGUSTUS MATTHIESSEN, F.R.S., Lecturer on Chemistry in St. Bartholomew's Hospital, and C. R. A. WRIGHT, B.Sc. Received May 6, 1869.

It has been shown that when narcotine is heated with an excess of concentrated hydrochloric or hydriodic acid, one, two, or three molecules of methyl are successively eliminated, and a series of new bases homologous with narcotine obtained. It appeared interesting to see if any similar reactions took place with morphia; and for this purpose a quantity of that base, in a perfectly pure state, kindly furnished by Messrs. M'Farlane, of Edinburgh, was submitted to experiment. The purity of the substance was shown by the following analysis.

It was found that although crystallized morphia does not lose its water of crystallization in an ordinary steam drying-closet (*i. e.* slightly below 100°), yet it readily loses the whole when placed in a Liebig's drying-tube immersed in boiling water, dry air being aspirated over it.

\* Odontography, 1846, p. 602.

(1) 1·824 gramme of M'Farlane's morphia thus lost 0·111 gramme.  
 (2) 2·458 grammes                "                "                0·145                "  
 (3) 2·312                "                "                , after recrystallization from  
 boiling alcohol, lost 0·148 gramme.

	Calculated.		Found.		
			(I.)	(II.)	(III.)
H <sub>2</sub> O	18	5·94	6·09	5·90	6·40
C <sub>17</sub> H <sub>19</sub> NO <sub>3</sub>	285	94·06			
<hr/>	<hr/>	<hr/>			
C <sub>17</sub> H <sub>19</sub> NO <sub>3</sub> +H <sub>2</sub> O	303	100·00			

Combustions of morphia with oxide of copper and oxygen :—

(I.) 0·3015 gramme of M'Farlane's morphia, dried at 120°, gave 0·7950 carbonic acid and 0·1890 water.

(II.) Morphia recrystallized from boiling alcohol, and dried at 120° :—  
0·3635 gramme gave 0·9535 carbonic acid and 0·2230 water.

	Calculated.		Found.	
			(I.)	(II.)
C <sub>17</sub>	204	71·58	71·91	71·54
H <sub>19</sub>	19	6·66	6·97	6·81
N	14	4·91		
O <sub>3</sub>	48	16·85		
<hr/>	<hr/>	<hr/>		
C <sub>17</sub> H <sub>19</sub> NO <sub>3</sub>	285	100·00		

Morphia recrystallized from boiling alcohol, and dried below 100° :—  
0·3575 gramme gave 0·8780 carbonic acid and 0·234 water.

	Calculated.		Found.	
			(I.)	(II.)
C <sub>17</sub>	204	67·33	67·00	
H <sub>21</sub>	21	6·93		7·27
N	14	4·62		
O <sub>4</sub>	64	21·12		
<hr/>	<hr/>	<hr/>		
C <sub>17</sub> H <sub>19</sub> NO <sub>3</sub> H <sub>2</sub> O	303	100·00		

When morphia is sealed up with a large excess of hydrochloric acid (about 10 cub. centims. of ordinary acid, of about 35 per cent. HCl to each gramme of morphia), and heated to 140°—150° for two or three hours, on opening the tubes after cooling no gas is found to have been formed, nor is there any formation of chloride of methyl. The residue in the tube contains the hydrochlorate of a new base, differing considerably in its properties from morphia. It may be obtained in a state of purity by dissolving the contents of the tube in water, adding excess of bicarbonate of sodium (not the ordinary carbonate Na<sub>2</sub>CO<sub>3</sub>, nor caustic soda, as these hasten the decomposition of the precipitated base), and extracting the precipitate with ether or chloroform, in both of which the new base is readily soluble, whilst morphia is almost insoluble in both menstrua. On shaking up the ether

or chloroform solution with a very small quantity of strong hydrochloric acid, the sides of the vessel become covered with crystals of the hydrochlorate of the new base. These may be drained from the mother-liquor, washed with a little cold water, in which the salt is sparingly soluble, and recrystallized from hot water and dried on bibulous paper or over sulphuric acid. No difference in the result appeared to be produced by continuing the digestion at 150° for six or twelve hours. The new base may also be formed by digesting morphia and excess of hydrochloric acid under paraffin on the water-bath for some days.

This hydrochlorate contains no water of crystallization. After drying in the water-bath, it yielded the following results on combustion with chromate of lead and oxygen:—

- (I.) 0·4300 gramme gave 1·0600 carbonic acid and 0·237 water.
- (II.) Sample (I.), recrystallized, and again dried in water-bath. 0·3270 gramme gave 0·8045 carbonic acid and 0·1830 water.
- (III.) 0·3830 gramme, burnt with soda-lime, gave 0·1240 metallic platinum.
- (IV.) 0·4720 gramme, burnt with soda-lime, and the ammonia estimated volumetrically, gave 0·0234 nitrogen.
- (V.) 0·4680 gramme, precipitated by nitrate of silver and nitric acid, gave 0·2170 chloride of silver.
- (VI.) 0·3410 gramme, burnt with lime, gave 0·1645 chloride of silver.

	Calculated.		Found.					
	(I.)	(II.)	(III.)	(IV.)	(V.)	(VI.)		
C <sub>17</sub>	204	67·22	67·23	67·10				
H <sub>18</sub>	18	5·93	6·12	6·21				
N	14	4·61			4·60	4·95		
O <sub>2</sub>	32	10·54						
Cl	35·5	11·70					11·50	11·93
C <sub>17</sub> H <sub>17</sub> NO <sub>2</sub> HCl	303·5	100·00						

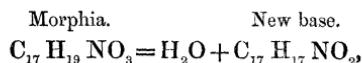
From a solution of the hydrochlorate in water, bicarbonate of sodium precipitates a snow-white non-crystalline mass, which speedily turns green on the surface by exposure to air, and is therefore difficult to obtain dry in a state of purity. The following combustion of a portion washed with water, and dried at 100° as rapidly as possible, shows that this precipitate is the base itself.

0·3310 gramme gave 0·9250 carbonic acid and 0·1830 water.

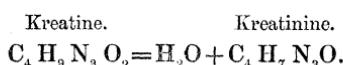
	Calculated		Found.
	(I.)	(II.)	
C <sub>17</sub>	204	76·40	76·22
H <sub>17</sub>	17	6·37	6·15
N	14	5·24	
O <sub>2</sub>	32	11·99	
C <sub>17</sub> H <sub>17</sub> NO <sub>2</sub>	267	100·00	

This substance was free from chlorine, as shown by its giving no precipitate with nitrate of silver after heating with nitric acid.

It hence appears that the new base is simply formed from morphia by the abstraction of the elements of water.



the reaction under the influence of hydrochloric acid being perfectly analogous to that by which kreatine, under the influence of strong acid, splits up into water and kreatinine.



We propose to call the new base apomorphia, for reasons given subsequently.

When the hydrochlorate of apomorphia in a moist state is exposed to the air for some time, or if the dry salt is heated, it turns green, probably from oxidation, as the change of colour is accompanied by an increase of weight. The base itself, newly precipitated, is white, but it speedily turns green on exposure to air. The green mass is partly soluble in water, communicating to it a fine emerald colour—in alcohol yielding also a green, in ether and benzole giving a magnificent rose-purple, and in chloroform producing a fine violet tint.

The following Tables show the most marked properties and reactions of apomorphia as contrasted with morphia.

	Water.	Alcohol.	Ether.	Chloroform.
Morphia .....	Almost insoluble.	Sparingly soluble cold, more soluble boiling.	Almost insoluble.	Almost insoluble.
Apomorphia ...	Slightly soluble, especially if charged with carbonic acid.	Soluble.	Soluble.	Soluble.

The following comparative reactions were made with solutions containing each 1 per cent. of the hydrochlorate of the base :—

Reagent.....	Caustic Potash.	Ammonia.	Lime-water.	Bicarbonate of Sodium.	Strong Nitric Acid.	Neutral Ferric Chloride.
Morphia .....	No precipitate. Stronger solutions give a white precipitate readily soluble in excess, without undergoing decomposition.	No precipitate. Stronger solutions give a crystalline white precipitate, insoluble in excess.	No precipitate. Morphia dissolves readily in lime-water.	No precipitate. Stronger solutions yield a white unalterable precipitate slightly soluble in excess.	Yellow orange-colour, almost bleached on warming.	Greenish-blue colour. Morphia alone gives a pure blue colour.
Apomorphia .....	White precipitate, soluble in excess, speedily blackening.		White precipitate, soluble in excess, slowly darkening.	White precipitate, slightly soluble in excess, turning green.	Blood-red colour, becoming paler on warming.	Dark amethyst-colour.
Reagent.....	Bichromate of Potassium.	Nitrate of Silver.	Iodide of Potassium.	Platinic Chloride.	Mercuric Chloride, Phosphate of Sodium, Oxalate of Ammonium.	
Morphia .....	—	—	Very slowly reduced.	—	The morphia precipitates with these reagents are much more soluble than the corresponding apomorphia ones.	
Apomorphia .....	Dense yellow orange precipitate, soon decomposing.	Dark-red coloration.	Quickly reduced, even in the cold.	White non-crystalline precipitate, speedily becoming green.	Yellow precipitate decomposes on warming.	

The physiological effects of apomorphia are very different from those of morphia; a very small dose produces speedy vomiting and considerable depression, but this soon passes off, leaving no after ill effects,—facts of which we have repeatedly had disagreeable proof while working with it.

Dr. Gee is now studying these effects, and has found that  $\frac{1}{10}$  of a grain of the hydrochlorate subcutaneously injected, or  $\frac{1}{4}$  grain taken by the mouth, produces vomiting in from four to ten minutes. Our friend Mr. Prus allowed himself to be injected with  $\frac{1}{10}$  grain, which produced vomiting in less than ten minutes. From Dr. Gee's experiments on himself and others, he concludes that the hydrochlorate is a non-irritant emetic and powerful anti-stimulant. As from these properties it appears probable that it may come into use in medicine, we have called it apomorphia, rather than morphinine, to avoid any possible mistakes in writing prescriptions.

Apomorphia is likewise formed by heating morphia and dilute sulphuric acid (1 vol. acid to 8 or 10 of water) in sealed tubes to  $140^{\circ}$ – $150^{\circ}$  for three hours. It appears possible that the substance obtained by Arppe \*, subsequently named sulphonmorphide by Laurent and Gerhardt †, is an impure sulphate of apomorphia, as the formula deduced by these latter chemists from their analysis,  $C_{34}H_{36}N_2O_8S$ , is identical with that of this sulphate,  $(C_{17}H_{17}NO_2)_2H_2SO_4$ . They, however, considered it a species of amide. On repeating Arppe's experiments, we have obtained apomorphia from the product. The physical characters ascribed to sulphonmorphide (of becoming green on keeping, especially on heating, of communicating this green tint to water, and of solubility in caustic alkalies, producing a brown substance by decomposition) are precisely those of the hydrochlorate of apomorphia. It appears probable that the class of analogous bodies produced from other alkaloids by similar means, such as sulphonarcotide, may possibly be the sulphates of new bases. We propose to submit these to experiment, and to prosecute our researches on the opium bases.

On sealing up codeia with hydrochloric acid and digesting it at  $150^{\circ}$ , we find some permanent gas is evolved, probably chloride of methyl, in which case the new base, if any, will be morphia or apomorphia or their isomers, as codeia differs from morphia only by  $CH_2$ .

#### IV. "Researches into the Constitution of the Opium Bases. Part II.—On the Action of Hydrochloric Acid on Codeia." By AUGUSTUS MATTHIESSEN, F.R.S., Lecturer on Chemistry in St. Bartholomew's Hospital, and C. R. A. WRIGHT, B.Sc. Received June 2, 1869.

Codeia and morphia are, as is well known, homologous, only differing in composition by  $CH_2$ . Both of them contain one atom of hydrogen replaceable by organic radicals, from which it appears that methyl-morphia

\* 1845. Ann. der Chem und Pharm. vol. Iv. p. 96.

† Ann. de Chimie et de Phys. [3] vol. xxiv. p. 112.